EFFECT OF GRAIN SIZE DISTRIBUTION ON THE COLOUR DEVELOPED BY GLAZE PIGMENTS

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Recently much effort has been directed towards a rational selection of a wide palette of inorganic pigments. Many researchers and developments have been addressed both to systems characterized by an excellent chemical resistance, high refractoriness and ionic conductivity, useful properties to resist to the extreme chemical and thermal conditions encountered during glazing and enamelling processes and to systems characterized by constant and narrow grain size distribution to develop the best colour in the matrix. In order to obtain the required pigment physical properties and to optimize the grain size to the desired colour hue, the industry relies on a trial and error procedure.

This approach is no longer satisfactory and this work focuses on the optimization of the physical pigments properties by the Design Of Experiments (DOE) approach.

To this purpose three different industrial pigments have been chosen and wet milled for different times in order to obtain different grain size distributions (Figure 1).

Several different grain size distributions have been chosen for each pigment and have been added (2 wt%) to two different frits, deposited on a ceramic support and fired in an industrial cycle.



Figure 1. Grain size distribution of the three pigments chosen (a) Fe-Cr-Zn; Co-Zn-Cr-Al (b); (c) Cr-Co obtained by laser granulometry

Tile colours have been measured by UV spectroscopy and defined by Kubelka-Munk absorption and CIELab parameters. As an example, here we report the data obtained with the Fe-Cr-Zn pigment.

Fe-Cr-Zn Pigment	L*		a*		b*	
Milling time	Cryst.	Matt	Cryst.	Matt	Cryst.	Matt
As obtained	32,38	45,28	12,67	13,34	7,20	7,34
60′	34,93	43,93	14,03	15,01	8,54	9,68
90'	37,00	44,81	14,67	15,46	10,76	10,73

Table 1. L*, a*, b* values of the glazes obtained with the Fe.Cr.Zn pigment milled for different times



Figure 2. The Kubelka-Munk parameter for the Fe-Cr-Zn pigment in matt (a) and crystalline (b) glazes

The data show as the colour developed by the pigments has a different behaviour as a function of milling time depending on the frits used. In fact, the Kubelka Munk absorption increases in a matt frit (Figure 2a), while it decreases in a crystalline frit (Figure 2b) as the milling time is increased. In contrast, the CIELab values do not evidence this behaviour.

In the work the optimization of physical properties has been studied with a mixture design approach. It has been verified that the Design Of Experiment (DOE) approach is a suitable tool for identifying the significant factors that control the colouring process of glazed tiles. Moreover a mathematical model has been proposed and tested with good results.